tion, then the gain in stabilization in going from $\varphi = 24°$ to $\varphi = 0°$ is $(D_0 - D_e)$; if it is assumed that D varies as $\cos^n\varphi$, $(D_0 - D_e)$ is fortuitously almost independent of the exponent (at least for $n = 1, 2$, or 3), because $\cos 24°$ is not far from unity. $(D_0 - D_e)$, the gain in stabilization on returning to the planar form, is calculated to be about 10 kcal.mole^{-1}; if this estimate is at all reasonable, it indicates that the *net* barrier to rotation is only about 2 kcal.mole^{-1}, which is less than the uncertainties introduced by many of the assumptions. In any event, the net barrier would seem to be very small indeed. The value of the resonance energy itself, D_0, depends on the function assumed for the variation of D with φ; with a $\cos^2\varphi$ dependence, it is about 57 kcal.mole^{-1}, and with $\cos^3\varphi$ about 42 kcal.mole^{-1}. These numbers should be regarded, however, with considerable skepticism.

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The Crystal Structure and Phase Transformation of α-Cu2P2O7

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α-Cu2P2O7 is found to be of monoclinic symmetry with $a = 6·876$ (5), $b = 8·113$ (5), $c = 9·162$ (5) Å, $\beta = 109·54$ (6)° and $Z = 4$. The structure has been refined in space groups Cc and $C2/c$, and the latter is the preferred choice. The anion possesses a twofold axis and a P–O–P bond angle of 157°. The inner and outer P–O bonds of the anion are 1·58 and 1·53 Å respectively. A phase transformation is found to begin at 70°C and extends to above 100°C. The reflexions with their l index odd show diffuse temperature dependent streaks directed along [100] in this temperature range. The transformation thus appears to proceed by a positional disordering of bent pyrophosphate ions.

Introduction

Copper pyrophosphate is one of a series of crystallographically related pyro-compounds which have iso-structural high temperature phases (called β) and related low temperature phases (called α). These compounds have the generalized formula $M_2X_2O_7$ with M the cation and X an element showing a disposition for tetrahedral coordination with oxygen atoms. This series of compounds includes the mineral thortveitite, which is a pyrosilicate of Y and Sc (Cruickshank, Lynton & Barclay, 1962), the analogous Sc pyrogermanate (Goldschmidt, 1931), the pyroarsenates of Zn and Mg (Calvo & Neelakantan, 1967), the pyrovanadate of Cd (Au & Calvo, 1967) and a number of pyrophosphates. Among the pyrophosphates Mn (Lukaszewicz & Smaj-

kiewicz, 1961), Cu (Lukaszewicz & Nagler, 1961), Mg (Calvo, 1965a, 1967) and Zn (Calvo, 1965b) have been investigated crystallographically. Each of these pyrophosphates, except $Mn_2P_2O_7$, displays a reversible phase transformation and in each case the room temperature form is the α phase. The unit cell volume of the α phase is roughly double, quadruple and sextuple that of the conjugate β phase for Cu, Mg and Zn salts respectively. Further, in each case, the c axis is roughly doubled with a c-glide plane replacing the mirror plane of the β phase while the a axis is unchanged, doubled and tripled in the respective α phases. Details of the α–β $Cu_2P_2O_7$ transition have not previously been reported although Roy, Middleswarth & Hummel (1948) suggested some evidence existed for a phase transformation. The α–β $Mg_2P_2O_7$ transformation, however,

has been studied in some detail. Roy *et al.* (1948) investigated the differential thermal analysis (d.t.a.), thermal expansion and powder X-ray pattern and suggested that the transformation was of diffuse first order involving the coexistence of the α and β phases over a substantial temperature range. Specific heat measurements by Oetting & McDonald (1963) were consistent with these observations. Recently electron paramagnetic resonance (e.p.r.) experiments (Calvo, Leung & Datars, 1967) and single-crystal X-ray diffraction techniques (Calvo, 1967) have been employed to study this transformation. The α to β $Zn_2P_2O_7$ transformation has been studied by d.t.a. (Katnack & Hummel, 1958) and by e.p.r. (Chambers, Datars & Calvo, 1964). The crystal structure of the β phase is known (Calvo, 1965b) and that of α-$Zn_2P_2O_7$ is partially resolved (Robertson & Calvo, 1967a). At 132 °C this compound undergoes a first order phase transformation to an inhomogeneous phase which at 155 °C becomes the β phase. All the β forms, including β-$Cu_2P_2O_7$ (Robertson & Calvo 1967b), feature a linear P–O–P group since the anion lies on a center of symmetry in the $C2/m$ space group. This anion, however, appears to be linear only as a result of disorder since the central oxygen atom in each case shows an anomalously high anisotropic temperature factor.

Lattice parameters and the space group possibilities for $Cu_2P_2O_7$ were reported by Lukaszewicz & Nagler (1961) together with a suggestion that its structure was closely related to that of thortveitite, the mineralogical analogue of the β phase. Since the unit cell of α-$Cu_2P_2O_7$ appears to be a sub-multiple of the other α phases and each transforms by, in part, doubling the c axis with the appearance of a c-glide plane, it is possible that the elucidation of the structure and mechanism of the phase transition in $Cu_2P_2O_7$ will provide a key to the understanding of the remainder of the series.

The study of the crystal structures of these compounds can be expected to play a significant role in the study of chemical bonding in inorganic compounds. Cruickshank (1961) has discussed the nature of $d\pi$–$p\pi$ bonding and its relation to the central bond angle in those pyro-compounds where the anion $X_2O_7^{n-}$ is formed by the condensation of two tetrahedral XO_4, with X representing chlorine, sulphur, silicon or phosphorus. This discussion was based on a valence bond approximation for the anion and thus necessarily ignored the influence of the environment. From an assumed linear dependence of the bond lengths on the bond order he predicted the X–O bond lengths of the pyrophosphate for the central oxygen atom of the anion in sp, sp^2 and sp^3 hybridization.

The question of the existence of pyro anions with central bond angles of 180° has been explored by Liebau (1961). He regards it as unlikely that linear anions occur in silicate or phosphate systems. Levi & Peyronel (1935) reported linear pyrophosphate anions resulting from a space group constraint that placed the anion on the threefold axis. Recently infrared spectroscopy (Lazarev, 1962) indicated that ZrP_2O_7 undergoes a transformation at about 300 °C and thus this suggests the need for further crystallographic investigation. In $Na_4P_2O_7.10H_2O$ (McDonald & Cruickshank, 1967) and β-$Ca_2P_2O_7$ (Webb, 1966) the P–O–P groups are not linear. The results reported below indicate that linear pyrophosphate anions are not stable and only appear so in the β phase as a result of a disordering.

Experimental

Crystals of $Cu_2P_2O_7$ were prepared by the reaction of a slight excess of an aqueous solution of $Na_4P_2O_7$ with an aqueous solution of $CuSO_4$. The precipitate was filtered, dried and heated to 1200 °C in an open Vycor tube. Upon cooling the melt slowly, small blue-green crystals were obtained. Some crystals were found to be twinned on the (110) face but single crystals could be selected. Lattice parameters for α-$Cu_2P_2O_7$ were obtained from a least-squares fit of 39 lines of a Debye–Scherrer photograph taken with Cu $K\alpha$ radiation. The parameters obtained are $a = 6.876$ (5), $b = 8.113$ (5), $c = 9.162$ (5) Å and $\beta = 109.54$ (6)°, where the wavelengths for α_1 and α_2 components of the radiation were taken from *International Tables for X-ray Crystallography* (1962). These lattice parameters are similar to those reported by Lukaszewicz & Nagler (1961) whose density value confirmed that the unit cell contained 4 molecules. Photographs of single crystals showed that reflexions indexed as hkl with $h + k$ odd were systematically absent, as were also those indexed as $h0l$ with l odd.

Weissenberg photographs containing hkn type reflexions with $n = 0$, 1 and 2 were recorded with Cu $K\alpha$ radiation for an irregularly shaped crystal of dimensions approximately $0.08 \times 0.08 \times 0.40$ mm³ where the c axis paralleled the long dimension. This crystal was also used to obtain $0kl$ data on the precession camera and $hk0$ data collected with a manual diffractometer. Both sets were taken with Mo $K\alpha$ radiation. The diffractometer data were measured with a Geiger tube using an ω scan, with background corrections applied from measurements made at $|\Delta\omega| \simeq 3°$ on either side of the peak of the reflexion. Zirconium filters were used to reduce the intensity of each reflexion so that the applied dead time corrections were less than 15% of the measured intensity. A second crystal, having approximate dimensions $0.10 \times 0.10 \times 0.05$ mm³, was used to obtain data of the type hnl with $n = 0$, 1, 2, 3, and 4 using Mo $K\alpha$ radiation and the Weissenberg camera. All these data were recorded at room temperature $(25 \pm 5 °C)$.

The intensities of the reflexions on the photographic films were visually estimated and all the data were corrected for the Lorentz and polarization effects. Since the linear absorption coefficients are 100 cm⁻¹ and 160 cm⁻¹ for Mo $K\alpha$ and Cu $K\alpha$ radiation respectively, absorption corrections were applied using assumed

cylindrical and spherical shapes for the crystal where appropriate.

A trial structure for α-$Cu_2P_2O_7$ was derived from the structure obtained for β-$Cu_2P_2O_7$.* In β-$Cu_2P_2O_7$ the anion contains a mirror plane and a twofold axis and the cations lie on a second twofold axis. The $\varrho(x,z)$ electron density maps showed considerable spread of the Cu^{2+} ions in a direction parallel to the a axis and the anisotropic thermal parameters for the central oxygen atom indicated a large disorder in the direction of the b axis. The trial structure for the $C2/c$ space group was so chosen that the central oxygen atom of the anion lay on the twofold axis and so that the cations were related by a center of symmetry but displaced along the a axis from their positions in the β phase. The Cu ion positions were refined until no further improvement in the residual,

$$R_2 = \Sigma[\{|F_o|_H - |F_c|_H\}^2 \omega_H](\Sigma\, \omega_H|F_o|_H^2)^{-1},$$

with ω = the weight, could be obtained. The central oxygen atom was then displaced alternately up and down the b axis, and all the atomic positions refined by a full-matrix least-squares precedure. The program used was written by J. S. Stephens of this laboratory. The proper direction for the displacement of the central oxygen atom was found by noting which trial structure gave the better agreement. The refinement of the structure in space group Cc was carried out in a similar manner. Initial refinement (Robertson, 1965) was started with only 350 reflexions by determining those displacements of Cu and P atoms from their β-phase coordinates that led to the best agreement. The oxygen atoms were readily found and all the parameters were refined in the centric space group but the refinement in the Cc space group led to P–O(P) bond lengths of 1·38 and 1·80 Å while the terminal bond lengths varied from 1·42 to 1·84 Å. After the remaining data were measured and added to the refinement of the non-centric structure it diverged primarily as a result of large oxygen atom displacements. The oxygen atoms were then placed in those positions found in the $C2/c$ space group and these refined in space group Cc. This led to atomic positions that differed by values ranging from 0·05 to 0·3 Å from those found in the centric space group. After absorption corrections were applied, these coordinates were used as initial parameters for the final cycles of refinements.

Initially, both unit and $1/\sigma^2$ weighting schemes were used, where σ is the estimated standard deviation of a given reflexion. After convergence had been obtained in both space groups, new weights, w, were calculated so as to satisfy a criterion suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) that $w^{-1} = C_0 + C_1F_o + C_2F_o^2 + C_3F_o^3$ where the C's are chosen so that the average value of $w\Delta^2$ should be independent of F_o. Unobserved reflexions whose calculated value was less than the minimum observed value were con-

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* Pertinent structural data for β-$Cu_2P_2O_7$ are given in the Appendix.

sidered to be in agreement and left out of the refinement. Otherwise, F_o for these reflexions was taken as $0.70 \times$ (minimum F_o). The final value of the crystallographic discrepancy index

$$R_1 = (\Sigma\, ||F_o|_H - |F_c|_H|)(\Sigma\, |F_o|_H)^{-1}$$

is 0·097 in $C2/c$ and 0·098 in Cc, whereas the values of the residuals, R_2, are 0·143 and 0·135 respectively.

The atomic parameters obtained for both space groups are compared in Tables 1 and 2. Only the x coordinates of the Cu ions and O_{III} in Cc deviate significantly from those in $C2/c$. Further, only five of the eleven atoms have positive definite thermal parameters in the lower symmetry space group (see Table 2). In total the $C2/c$ space group is to be preferred since the lower R values for Cc are obtained with an unrealistic model.

Table 1. *Positional atomic parameters for* α-$Cu_2P_2O_7$

(e.s.d.'s in parenthesis)

(a) In space group $C2/c$

	x/a	y/b	z/c
Cu	−0·0180 (1)	0·3132 (1)	0·5070 (1)
P	0·1979 (2)	0·0077 (3)	0·2060 (2)
O_I	0	0·0471 (18)	$\frac{1}{4}$
O_{II}	0·3764 (8)	−0·0026 (9)	0·3625 (7)
$O_{III}(c)$	0·2213 (8)	0·1572 (7)	0·1135 (6)
$O_{III}(t)$	0·1778 (10)	−0·1526 (7)	0·1189 (7)

(b) In space group Cc

	x/a	y/b	z/c
Cu(1)	−0·0130 (3)	0·3126 (4)	0·5070 (18)
Cu(2)	0·0225 (3)	−0·3137 (4)	0·4930 (2)
P(1)	0·1977 (9)	0·0088 (7)	0·2054 (7)
P(2)	−0·1980 (9)	0·0066 (6)	0·2938 (6)
O_I	0·0000 (32)	0·0473 (22)	0·2500 (34)
$O_{II}(1)$	0·3744 (21)	−0·0002 (17)	0·3618 (16)
$O_{II}(2)$	−0·3776 (25)	−0·0065 (26)	0·1371 (23)
$O_{III}(1c)$	0·2291 (21)	0·1513 (14)	0·1154 (15)
$O_{III}(2c)$	−0·2129 (25)	0·1650 (17)	0·3864 (15)
$O_{III}(1t)$	0·1890 (23)	−0·1538 (19)	0·1217 (17)
$O_{III}(2t)$	−0·1650 (25)	−0·1545 (19)	0·3832 (15)

Traditional crystallographic methods are unable to substantiate the adequacy of the trial structure chosen for the refinement in the non-centrosymmetric space group, however. Recent nuclear magnetic experiments have removed any lingering doubts concerning the space group of α-$Cu_2P_2O_7$. At room temperature only one resonance line due to the nuclear moment of phosphorus was obtained, and further the shift of this resonance relative to that of phosphorus in $Mg_2P_2O_7$ was found to be isotropic. This result is consistent only if the two ends of the anion are symmetry related and, therefore, the space group must be $C2/c$. In general, the variation of the line position with the orientation of the crystals relative to a fixed magnetic field direction would be described by a second order tensor and, therefore, the isotropic nature of the resonance must be accidental. It is comforting that at 77°K, where the P nuclear resonance in $Cu_2P_2O_7$ is further shifted owing to the enhanced alignment of the paramagnetic Cu^{2+}, that the line width is sufficiently reduced (2 gauss) that

a small anisotropy could be measured as the orientation of the magnetic field is changed in the *ab* crystallographic plane.

Table 3 lists the 1112 independent structure factors recorded together with their calculated values, using the atomic parameters for space group $C2/c$ and $C_0 = -1\cdot607$, $C_1 = 0\cdot4518$, $C_2 = -5\cdot06 \times 10^{-3}$ and $C_3 = 12\cdot43 \times 10^{-5}$ in the expression defining the weights.

The scattering curves used were those for Cu^{2+}, P and O^- taken from *International Tables for X-ray Crystallography* (1962) except that corrections for anomalous dispersion were applied to the Cu^{2+} curve. These corrections were significant only for the data taken with Cu $K\alpha$ radiation.

The phase transformation

A limited series of photographs was taken as a function of temperature to determine the transition temperature and whether the high and low temperature phases co-existed as seemed to be the case in $Mg_2P_2O_7$. Several photographs were taken with a Nonius high–low temperature camera at various crystal orientations and temperatures in the range from room temperature to 110 °C. Those reflexions common to both phases, that is, reflexions with the *l* index even based on the α unit cell, showed modest changes in their intensities but no change in spot shape. The reflexions indexed by *l* odd, however, developed diffuse streaks. This diffuseness could be seen at 66 ± 1 °C* and reached a

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* The estimated errors measure the precision but not the accuracy. A systematic error of up to $+5$ °C is possible because of the difficulty in calibrating the temperature difference between the crystal and the position of the thermocouple.

maximum in their intensity between 69 and 75 °C. Beyond 75 °C they became progressively weaker. At 110 °C the diffuseness had faded to a point where exposures for more than three hours for 60° angular range in the Weissenberg photographs were required to attain sufficient contrast to observe these streaks.

A zero level Weissenberg photograph was taken of a crystal aligned on its *c* axis with the screen opening set so as to allow the emission of both $l = 0$ and $l = 1$ layer lines. All the diffuse streaks could be simultaneously aligned with the Weissenberg net lines, indicating that the streaks extended only in one direction, that is along **a**.* Their length was $0\cdot07 \pm 0\cdot015$ Å^{-1} or about $\frac{1}{2}a^*$, with a width of $0\cdot015 \pm 0\cdot005$ Å^{-1} and centred at the position expected for the Bragg peak. The intensity of the diffuse scattering was remarkably flat over its whole length throughout the entire temperature range.

The Bragg peak disappeared at 69 ± 1 °C. Over the three degrees that the diffuse scattering and the Bragg peak co-existed the edge of the latter did not fade continuously into the diffuse scattering, but in fact, seemed to remain distinct. The length of the streaks remained constant in the temperature range, 66 to about 85 °C, where their shape could be studied. The detailed intensity profiles as a function of temperature are currently under investigation.

Description of the structure

The structure of α-$Cu_2P_2O_7$ is closely related to the other members of this series. The cations are found in irregular octahedral coordination with oxygen atoms as can be seen in Fig. 1. The major distortion from regularity consists of an elongation of the two metal–

Table 2. *Thermal atomic parameters for* α-$Cu_2P_2O_7(\times 10^4)$

(e.s.d.'s in parenthesis)

(*a*) In space group $C2/c$

	U_{11}*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	110 (3)	138 (5)	111 (3)	5 (3)	−19 (2)	−1 (4)
P	66 (4)	157 (9)	84 (5)	−18 (6)	15 (4)	17 (7)
O_I	111 (24)	645 (82)	305 (44)	—	86 (28)	—
O_{II}	83 (12)	327 (38)	161 (17)	−1 (22)	−13 (13)	−6 (27)
$O_{III}(c)$	149 (15)	95 (17)	122 (14)	−22 (18)	32 (12)	18 (23)
$O_{III}(t)$	221 (21)	137 (19)	169 (19)	−7 (24)	−9 (17)	−5 (30)

(*b*) In space group Cc

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	103 (7)	152 (12)	191 (12)	−9 (16)	−15 (8)	−90 (21)
Cu(2)†	108 (7)	135 (7)	69 (4)	17 (14)	−19 (6)	74 (18)
P(1)	66 (16)	199 (30)	116 (15)	−1 (29)	52 (13)	−46 (35)
P(2)	75 (16)	159 (23)	71 (10)	83 (22)	−30 (11)	−105 (30)
O_I	178 (31)	720 (84)	364 (53)	−328 (77)	184 (37)	−169 (38)
$O_{II}(1)$†	85 (42)	115 (33)	104 (36)	20 (142)	−4 (31)	−158 (179)
$O_{II}(2)$	86 (42)	695 (140)	237 (68)	15 (210)	−78 (40)	−148 (294)
$O_{III}(1c)$†	125 (31)	37 (26)	133 (39)	125 (37)	43 (35)	90 (65)
$O_{III}(2c)$†	234 (46)	128 (39)	93 (39)	197 (46)	48 (41)	26 (46)
$O_{III}(1t)$†	208 (27)	308 (35)	181 (50)	−359 (31)	43 (38)	−324 (78)
$O_{III}(2t)$†	298 (51)	222 (49)	93 (50)	−287 (43)	−36 (39)	−186 (68)

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* These values were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where β_{ij}'s appear as a temperature effect through exp $[-(\beta_{11}h^2 + 2\beta_{12}hk\ldots)]$ in the structure factor expression and b_i are the reciprocal lattice vectors.

† Non-positive definite.

oxygen atom bonds lying nearly perpendicular to the b axis. The two remaining pairs of oxygen ligands lie above and below this plane and are rotated about the b axis in opposite directions from their 'regular' position. These cation octahedra share edges to form a pseudo-hexagonal network extended in the (001) plane. Adjacent sheets of these octahedra are joined by the pyrophosphate anions. These anions, consisting of corner shared PO_4^{3-} tetrahedra, form $P_2O_7^{4-}$ groups as shown in Fig. 2. They share two of their terminal oxy-gen atoms on each side with one sheet and the third with the adjacent sheet. The P–O–P angle is approximately 157°, the central P–O bond is 1·576 Å, and the average terminal P–O bond is 1·525 Å when uncorrected for the effects of the thermal motion. The minimum corrections to these bond lengths due to thermal motion would be 0·007 and 0·001 Å respectively (Busing & Levy, 1964). The predicted values are 1·58 and 1·53 Å for the inner and outer P–O bond lengths when the central oxygen atom is sp hydridized

Table 3. *Observed and calculated structure factors* ($\times 10$) *for* α-CuP_2O_7

Unobserved reflexions were assigned F_{OBS} values corresponding to the minimum possible observable value and are designated with an asterisk.

and 1·64 and 1·51 Å when it is sp^2 hybridized (Cruick-shank, 1961). These pertinent bond lengths found for α-Cu$_2$P$_2$O$_7$ are listed in Table 4. The important bond angles of this structure are found in Table 5.

The short (equatorial) cation–oxygen atom bond lengths are found to lie between 1·90 and 1·99 Å with an average value of 1·95 Å, whereas the long (axial) cation–oxygen atom bond lengths are 2·32 and 2·95 Å. Long cation ligand bond distances are characteristic of divalent Cu. In β-Cu$_2$P$_2$O$_7$ the analogous axial bond lengths are 2·58 Å, which is nearly the mean of the two axial bond lengths in the α structure.
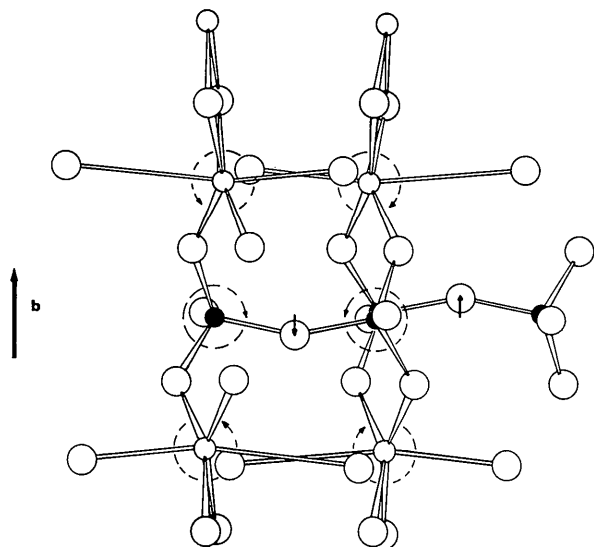

Fig. 1. The structure of α-Cu$_2$P$_2$O$_7$ viewed in the *bc* plane. The relationship between the bent P–O–P group and the twist imposed on the CuO$_6$ group is shown. This distortion from $C2/m$ space group symmetry gives rise to the *c*-glide plane and doubled *c* axis. The oxygen atoms, phosphorus atoms and Cu ions are represented by large open circles, filled small circles and by small open circles respectively.
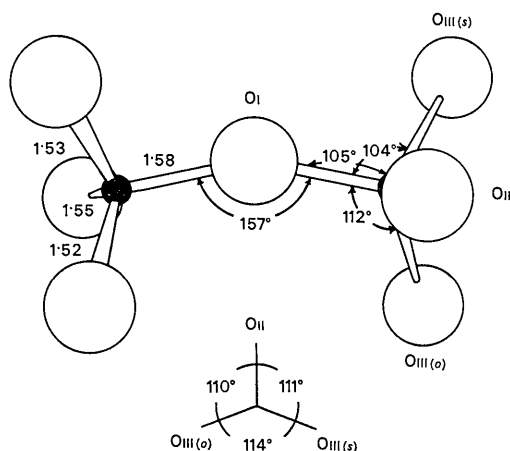

Fig. 2. A view of the pyrophosphate anion in α-Cu$_2$P$_2$O$_7$. The oxygen atoms of type III that lie on the same side of the *c*-glide plane as O$_I$ are designated (c) and those on the opposite side (t). The large circle represents oxygen atoms and the filled small circles are phosphorus atoms.

Discussion

The fact that *l*-odd type reflexions show diffuseness in the [100] direction means that the structure loses long range periodicity in that direction. Long range order in the *bc* plane is maintained by the same mechanism that gives rise to the *c*-glide plane and thus might be a feature common to all the structures in this series. This glide plane can be considered to be derived from the $C2/m$ symmetry of the β phase by a displacement of a central oxygen atom parallel to the *b* axis out of collinearity with the phosphorus atoms of the same

Table 4.

(*a*) Molecular geometry of the P$_2$O$_7^{4-}$ ion in α-Cu$_2$P$_2$O$_7$

(e.s.d.'s are in round brackets and the analogous β values in clamps)

Distances		
P–P	3·086 (4) Å	
P–O$_I$	1·576 (7)	{1·544}
P–O$_{II}$	1·547 (7)	{1·508}
P–O$_{III}$(c)	1·519 (7)	{1·503}
P–O$_{III}$(t)	1·508 (7)	
O$_I$–O$_{II}$	2·478 (14)	
O$_I$–O$_{III}$(c)	2·439 (15)	
O$_I$–O$_{III}$(t)	2·559 (15)	
O$_{II}$–O$_{III}$(c)	2·529 (15)	
O$_{II}$–O$_{III}$(t)	2·508 (15)	
O$_{III}$–O$_{III}$(t)	2·534 (15)	
Angles		
P–O–P'	157°	{180}
O$_I$–P–O$_{II}$	105	{105}
O$_I$–P–O$_{III}$(c)	104	{109}
O$_I$–P–O$_{III}$(t)	112	—
O$_{II}$–P–O$_{III}$(c)	111	{111}
O$_{III}$(c)–P–O$_{III}$(t)	114	{112}

(*b*) Molecular geometry about the cations in α-Cu$_2$P$_2$O$_7$

Cu–O$_{II}$	1·990 (6) Å
Cu–O$_{II'}$	1·968 (6)
Cu–O$_{III}$(c)	1·907 (6)
Cu–O$_{III}$(t)	1·935 (6)
Cu–O$_{III}$ (c)	2·322 (6)
Cu–O$_{III}$ (t)	2·947 (6)

Table 5. *Angles subtended at the terminal oxygen atoms by its ligands in* α-Cu$_2$P$_2$O$_7$

		Angle
At O$_{II}$	Cu–O$_{II}$–Cu'	101°
	P—O$_{II}$–Cu	126
	P—O$_{II}$–Cu'	131
	sum	358
At O$_{III}$(c)	Cu–O$_{III}$(c)–Cu'	102
	P—O$_{III}$(c)–Cu	124
	P—O$_{III}$(c)–Cu'	130
	sum	356
At O$_{III}$(t)	Cu–O$_{III}$(t)–Cu'	104
	P—O$_{III}$(t)–Cu	110
	P—O$_{III}$(t)–Cu'	143
	sum	357

anion. In Fig. 1 one of these oxygen atoms (O_I) in the pyrophosphate is displaced parallel to $+\mathbf{b}$. The terminal oxygen atoms will then rotate about an axis passing through the phosphorus atoms which is perpendicular to both the b axis and the P–P vector. This will preserve the pseudo threefold axis which relates the terminal oxygen atoms. The two ends of the anion, however, will rotate in opposite directions, maintaining a twofold axis through the central oxygen atom. At each end the anion is bonded through oxygen atoms of type III to a pair of cation octahedra which would be on the same twofold axis of the β phase. These two cation pairs are displaced by one unit cell along $\mathbf{c}$ of the β phase. The net effect of these rotations will be, for rigid octahedral groups, that the anion groups adjacent along $\mathbf{c}$ must be displaced oppositely along $\mathbf{b}$ to give a consistent displacement to the terminal oxygen atoms and this gives rise to the c-glide plane and doubled periodicity along the $\mathbf{c}$ direction. This effect is illustrated in Fig. 1.

In contrast with the high stability of the periodicity along the $\mathbf{c}$ direction, the structure is seen to be susceptible to a special type of error propagated in the $\mathbf{a}^*$ direction. If the direction of the displacement of the pyrophosphate ion and the cations in one layer perpendicular to the $\mathbf{a}^*$ direction are reversed relative to their β phase positions only modest structural changes in cation oxygen bond distances are required at the boundary between the layers (Fig. 3). In particular the long Cu–O bond distances become identical and equal to their average value, 2·63 Å, and the remaining Cu–O bonds affected by this disordering become 1·96 and 2·00 Å compared with 1·97 and 1·99 Å in the ordered α structure. Adjacent layers with such an error are entirely equivalent, analytically, to a stacking error of $\frac{1}{2}c$. If such stacking errors are randomly distributed

with a mean probability of $\frac{1}{2}$, the structure will appear to have $C2/m$ symmetry with the c axis halved and the anion averaged so as to appear linear. This would result in the β structure, in agreement with the structure found (Robertson & Calvo, 1967b), that is, the average of the positions of two equivalent α-$Cu_2P_2O_7$ unit cells, one with origin at 0,0,0 and the other 0,0,$\frac{1}{2}$.

Since relatively small differences in the long Cu–O bonds would differ by small amounts in energy, it can be expected that the sense of adjacent layers could easily be reversed and thus yield a stacking fault. As the temperature is raised the number of these stacking errors increases until each sense for a layer, relative to a chosen positive direction at an arbitrary origin, is randomly distributed in the structure. At this point the structure would have become the β phase with the anion positionally disordered rather than vibrationally or rotationally disordered. This model for the transformation predicts the appearance of diffuse streaks directed along the $\mathbf{a}^*$ direction.

This phase transition seems to be of second order thermodynamically although of an inhomogeneous type. These experiments show that there is no volume discontinuity and further that the electron density changes continuously but that the symmetry changes abruptly at the transition from Cc to $C2/m$. Landau & Lifshitz (1962) defined a second order phase transformation in these terms and derived a number of group theoretical consequences resulting from the fact that Gibbs free energy in both phases must be a function invariant to the symmetry group of the phases involved. Despite that fact that the present space group satisfies all the criteria necessary for a homogeneous second order transformation it is inhomogeneous. Similar examples occur in magnetic systems and have been discussed by Haas (1965) and Dimmock (1963).
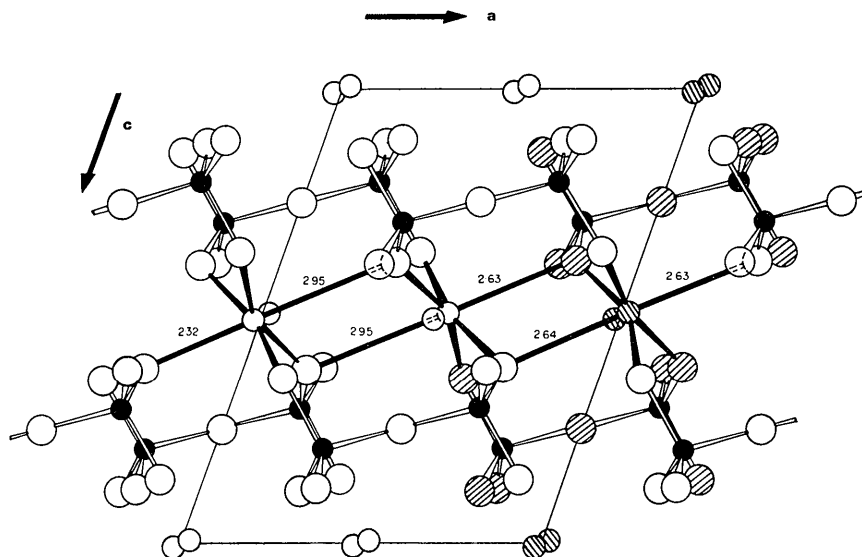

Fig. 3. The partially disordered α-$Cu_2P_2O_7$ structure projected down the b axis. The third layer (hatched) is disordered by a stacking error of $\frac{1}{2}c$ with respect to the first two layers. The axial Cu–O_{III} bond distances are shown. The filled circles represent phosphorus atoms, the small open or hatched circles Cu^{2+} and the large circles oxygen atoms.

A comparison of the value found for the P–O–P angle among the pyrophosphates indicates that an environment effect exists. This angle is near 130° in $Na_4P_2O_7$.$10H_2O$ (McDonald & Cruickshank, 1967), 144° in α-$Mg_2P_2O_7$ (Calvo, 1967) and 157° in the present case. An indication of some electron delocalization from the anion to the cation is provided by an examination of the detailed environment about each oxygen atom. In particular, Table 5 gives the angles at each of the oxygen atoms to the two metal ions and the phosphorus atom to which it is ligated. In each case, the sum of the angles about each of the oxygen atoms totals nearly 360° and thus indicates a nearly planar distribution of the four species. Thus, the terminal oxygen atoms can be considered to have some sp^2 hybridization which might be expected to effect the total number of electrons in the anion.

In summary, the space group $C2/c$ is favored for α-$Cu_2P_2O_7$. The P–O–P group of the anion is bent. The diffuse scattering indicates that the β phase has bent, but positionally disordered anions. This point will be discussed further when the detailed investigation of the diffuse scattering is reported.

Appendix

The pertinent structural data for β-$Cu_2P_2O_7$ at 100 °C are:

$a = 6\cdot827$ (8) Å
$b = 8\cdot118$ (10)
$c = 4\cdot576$ (6)

$\beta = 108\cdot85$ (10)°
$Z = 2$
Space group $C2/m$
$\mu = 100$ cm^{-1} (Mo $K\alpha$ radiation used throughout).

The total number of reflexions is 614 and the final value of R_1 is 0·135, whereas R_2 is 0·141.

The atomic coordinates with origin at the center of symmetry lying on the twofold axis through the cations are:

	x/a	y/b	$z/2c$
Cu	0	0·3121 (2)	$\frac{1}{2}$
P	0·2001 (4)	0	0·2059 (3)
O_I	0	0	$\frac{1}{4}$
O_{II}	0·3750 (9)	0	0·3574 (7)
O_{III}	0·2037 (1)	0·1537 (10)	0·1150 (7)

and the important bond lengths and angles are:

P–O_I	1·544 (5) Å	O_I–P–O_{II}	105°
P–O_{II}	1·508 (15)	O_I–P–O_{III}	109
P–O_{III}	1·503 (15)	O_{II}–P–O_{III}	111
		O_{III}–P–O_{III}	112
Cu–O_{II}	2·008 (6)		
Cu–O_{III}	1·936 (10)		
Cu–O_{III}'	2·578 (10)		

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